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Homopolymers of 2,2,2-trifluoroethyl methacrylate (TFEMA) and 2,2,2-trichloroethyl methacrylate (TCEMA) and copolymers with methyl α-chloroacrylate (MCA) of a range of composition were synthesized. Radiolysis of copolymers are initiated by dissociative electron capture by the halogen atom. GC-MS analysis of volatile products show that the poly(TFEMA) tend to depolymerize but not poly(TCEMA). Some of the polymers merit further investigations for E-beam or X-ray lithographic applications.

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Radiolysis of Resist Polymers. III.

Copolymers of Methyl-α-Chloroacrylate and Trihaloethylmethacrylates

By

G.N. Babu, P.H. Lu, S.L. Hsu, and James C.W. Chien

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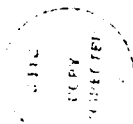Amherst, Massachusetts 01003

August 1983

Radiolysis of Resist Polymers.III. Copolymers of

Methyl-α-Chloroacrylate and Trihaloethylmethacrylates

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Abstract

Homopolymers of 2,2,2-trifluoroethyl(methacrylate) (TFEMA) and 2,2,2-trichloroethyl(methacrylate) (TCEMA) and copolymers with methyl-α-chloroacrylate (MCA) of a range of composition were synthesized. The reactivity ratios were obtained; the two copolymerizations are close to ideal. Poly(MCA) has G_s = 7.4 and G_x = 0.9 by γ-radiolysis. On the other hand poly(TFEMA) and poly(TCEMA) have G_s values of 2.0 and 2.4, respectively, and G_x = 0. Radiolysis of copolymers are initiated to a large degree by dissociative electron capture by the halogen atoms in both comonomers as evidenced by the ESR spectra of radicals derived from them. There are germinal recombinations in irradiated poly(TFEMA) suggesting the presence of radicals in close proximity. This process is absent in the copolymers. GC-MS analysis of volatile products and other supporting evidence show that the TFEMA monomers tend to depolymerize but not the TCEMA. The radiolysis yields vary monotonically with the comonomer composition for the MCA-TFEMA system but the yields-composition relationship is not regular in the case of MCA-TCEMA copolymers. Four non-crosslinking systems were found to be potential radiation resists arranged in increasing order of promise are: poly(TFEMA) (G_s = 2.0, T_g = 70°); poly(TCEMA) (G_s = 2.7, T_g = 142°); and poly (94MCA-co-6TCEMA) (G_s = 2.7, T_g = 142°); and poly (68MCA-co-32TFEMA) (G_s = 3.0, T_g = 112°). These materials merit

further investigation for E-beam or x-ray lithographic applications. Mechanisms of radiolysis for these materials were discussed based on the ESR, GC-MS and radiolysis yield data.

Introduction

Recently, polymers highly sensitive to radiation have been sought for electron lithography applications. The advantages and limitations of evaluation by gamma radiolysis have been enumerated in papers I and II.[2,3] Poly(methyl-α-chloroacrylate) (poly(MCA)) has been found to have very high sensitivity to scission by radiolysis (G_s = 7.4)[2,4] but also showed definite tendency toward crosslinking (G_x = 0.9)[2,5]. It was reported that copolymers of MCA with MMA,[6] methacryloninitrile,[7] and terpolymers of MCA with MMA and hexylmethacrylate[5] of certain compositions have greater G_s values than PMMA and without discernible crosslinking. We found, however, that G_x values remain nonzero[2] for copolymers of MCA and MMA of all compositions but with a broad minimum of G_x between 72 and 38 mole % of MCA.

Poly 2,2,2-(trichloroethylmethacrylate) (poly(TCEMA)) was found to have G_s = 2.4 and G_x = 0,[3,8] but is said to crosslink at high dose. Copolymers of TCEMA and MMA of all compositions at low dose do not crosslink,[2] as one might expect from two non-crosslinking systems. Because G_s is large for TCEMA, it is worthwhile investigating its copo-

lymers with MCA to find copolymers with large G_s but $G_x = 0$. In this paper we present the results of radiolysis yields, ESR, and GS-MS of volatile products of copolymers of MCA-TCEMA and of MCA with 2,2,2-trifluoroethylmethacrylate (TFEMA).

Experimental Section

Materials. The synthesis of MCA and TCEMA have been given previously.[2,3] TFEMA was obtained by a similar procedure using trifluoroethanol and methacryloyl chloride.

Methods. The materials for copolymerization, polymer characterization, γ-radiolysis, determinations of G_s, G_x, and G_r, ESR, and GC-MS analysis of volatile radiolysis products are the same as given previously.[2]

Results and Discussion

Table I   Copolymerization and Properties of Copolymers.- Table I summarizes the results of copolymerizations with M_2 amd m_2 denoting the mole fraction of the trihaloethylmethacrylate monomer in the feed and copolymer, respectively. The copolymerization reactivity ratios are for the MCA/TFEMA system $r_1 = 0.48$, $r_2 = 0.82$; they are $r_1 = 0.50$, $r_2 = 0.82$

for the MCA/TCEMA system. The copolymer composition curves are given

Fig. 1,2 in Figures 1 and 2. The reactivity ratios are very similar for the two

systems. Apparently any differences in various steric and electronic

effects compensate for the two trihaloethylmethacrylate monomers. Also

the two copolymerizations are close to ideal and the comonomer contents

in the copolymer correspond closely to the feed compositions.

Table I. Copolymerization data and properties of copolymers

	Comonomer M_2	m_2^a	% conversion	T_g °C	$\overline{M}_n$ x 10^5	$\overline{M}_w$ x 10^5	$\overline{M}_w/\overline{M}_n$
TFEMA	0.30	0.29(0.31)	9.6	126	5.0	7.0	1.4
TFEMA	0.35	0.35(0.33)	8.4	117	4.9	7.5	1.5
TFEMA	0.60	0.60(0.64)	10.4	112	4.7	6.9	1.5
TFEMA	0.75	0.78(0.79)	6.8				
TFEMA	1.0	1.0		72	4.7	6.6	1.4
TCEMA	0.05	0.05(0.06)	8.4	142	5.1	8.0	1.6
TCEMA	0.15	0.24(0.22)	6.8	140	3.5	5.7	1.6
TCEMA	0.22	0.30(0.31)	9.6	136	2.5	4.3	1.7
TCEMA	0.60	0.63(0.64)	10.4				
TCEMA	1.0	1.0		132	1.5	2.3	1.6

[a]Comonomer content in copolymer obtained from elemental analysis for carbon,
t e value in parenthesis was obtained for elemental analysis for halogen.

The homo- and copolymers of TFEMA are soluble in acetone, aceto-
nitrile, chloroform and THF. Poly(TFEMA) has a rather low T_g of 72°.
The copolymers have T_g lying between the two homopolymers. The homo-
and co-polymers of TCEMA are soluble in chloroform, acetonitrile and
THF. The glass transition temperature of poly(TCEMA) is 132°.
Copolymers have T_g between this and 145° which is the T_g of poly(MCA).

Gamma Radiolysis

a. Yields.-The polymers were irradiated in a range of doses, D, and
$\overline{M}_n$ and $\overline{M}_w$ determined by GPC. The results were plotted in $\overline{M}^{-1}$ versus D

Fig. 3,4   to obtain G_s and G_x values [2,3] (Figures 3 and 4). For
poly(70MCA-co-30TCEMA) the molecular weights showed marked increase at
the highest dose (Figure 4c). The results of radiolysis yields are

Table II   given in Table II.

All the copolymers have reduced values of G_x as compared to G_x =
0.9 for poly(MCA). Two copolymers, poly(38MCA-co-62TFEMA) and
poly(94MCA-co-6TCEMA) have G_x = 0 and G_s greater than the homopolymers
of trihaloethylmethacrylates. In the case of TFEMA, G_s and G_x values
change monotomically with copolymer composition. In the case of TCEMA
the G_s has a minimum and G_x has a maximum in the vicinity of 30 mole %
of TCEMA.

Table II. Radiolysis Yields

Polymer	$G_{\underline{s}}$	$G_{\underline{x}}$	$G_{\underline{r}}$
Poly(70MCA-co-30TFEMA)	5.5	0.7	7.4
Poly(66MCA-co-34TFEMA)	4.4	0.3	6.8
Poly(38MCA-co-62TFEMA)	3.2	0	-
Poly(TFEMA)	2.0	0	3.2
Poly(94MCA-co-6TCEMA)	2.7	0	2.7
Poly(78MCA-co-22TCEMA)	2.1	0.1	4.8
Poly(70MCA-co-30TCEMA)	1.5	0.15	5.4
Poly(TCEMA)[3]	2.4	0	4.1
Poly(MCA)[2]	7.4	0.9	

b. ESR.-Gamma irradiated poly(MCA) and poly(MMA-co-MCA) of all compositions yielded a seven line ESR spectra,[2] which are shown by microwave saturation and effect of temperature to be due to two radicals $\sim\sim CH_2(Cl)\overset{\bullet}{C}(COOMe)$ (I) and $\sim\sim CH_2(COOMe)\overset{\bullet}{C}-CH_2\sim\sim$ (II). Therefore, the radiolysis was dominated by the dissociative electron capture by the α-Cl atom. On the otherhand γ-irradiated homo-and co-polymers of haloethylmethacrylates with MMA show the characteristic nine line ESR spectra of irradiated PMMA,[3] which is $\sim\sim CH_2(Me)\overset{\bullet}{C}(COOR)$ (III) where R is -CH$_2$CH$_2$X and X is F or Cl.

Fig. 5   Figure 5a shows that also to be true for R = -CH$_2$CF$_3$. The effect of microwave on ESR showed all the lines to saturate homogeneously (Figure

Fig. 6   6a). But the radicals have different rates of combination. Figure 7a

Fig. 7   showed that roughly about half of the radicals disappeared upon warming the irradiated poly(TFEMA) to 40°. There was very little change of ESR intensity between 40° and 54°, above which temperature the intensity decreases rapidly vanishing completely at 80°, i.e. near T_g. Similar behavior was observed with the radicals in the γ-irradiated poly(FEMA).[3] The disappearance of radicals between 25° and 40° may be attributed to geminal recombination processes.

The ESR spectra of γ-irradiated MCA-TFEMA copolymers are clearly due to radicals associated with both monomer units (Figure 5b). The lowest field line A and next to the highest field line H are not found in the ESR spectra of poly(MCA); they are due to radical III. The

other lines are the superpositions of resonances of radicals $\underset{\sim}{I}$, $\underset{\sim}{II}$ and $\underset{\sim}{III}$. These lines are inhomogeneously broadened (Figure 6b); whereas the other lines saturate differently supporting the above interpretation. The effect of temperature is also interesting (Figure 7b). We note that radical $\underset{\sim}{III}$ contributes only to lines A and H, all three radicals have intensities in lines B, C and D, whereas lines E, F, G are mostly due to radical $\underset{\sim}{II}$. The data suggests that at ambient temperature radical $\underset{\sim}{I}$ can be converted to radical $\underset{\sim}{II}$ and maybe also radical $\underset{\sim}{III}$. This is reasonable because $\underset{\sim}{I}$ is a reactive terminal radical whereas $\underset{\sim}{II}$ is a main chain radical.

The ESR spectra of γ-irradiated poly(94MCA-co-6TCEMA) is the same as that of poly(MCA). The only qualitative discernible difference is that the radical intensity in the copolymer remained virtually unchanged between 40° and 110° then rapidly decreases and vanishes at ca. 150°. In the homopolymer there were more complicated change of intensity of various lines with temperature.[2] It seems that all the terminal radical of type $\underset{\sim}{I}$ were largely converted to type $\underset{\sim}{II}$ main chain radical slightly above the ambient temperature in this copolymer. Furthermore, there were no clusters of radicals for geminal recombinations.

The ESR spectra of γ-irradiated copolymers with high TCEMA contents are more complicated as one might expect. The room temperature spectra of poly(78MCA-co-22TCEMA) is shown in Figure 8a. Above 50°

there is developed the additional line (A) at low field side and
another line H indicative of the appearance of radical $\underset{\sim}{III}$ (Figure $\underline{8b}$).
At higher temperatures the ESR spectra becomes purely that of species
$\underset{\sim}{III}$. The spectra showed the conversion to occur between 60° and 80°
with a doubling of intensity of most resonance lines before rapid
decline to zero at $\underline{ca}$. 120°. Therefore, in this system, there are no
clusters of radicals, the type $\underset{\sim}{I}$ and $\underset{\sim}{II}$ radicals are readily trans-
formed to type $\underset{\sim}{III}$ radical, and all radicals recombine at 20° below T_g of
the copolymer.

A small change of copolymer composition resulted in very signifi-
cant change in the ESR spectra. Poly(70MCA-$\underline{co}$-30TCEMA) has the lowest
$G_{\underline{s}}$ and highest $G_{\underline{x}}$ values of this copolymer system (Table II). Figure

Fig. 9 $\underline{9a}$ showed superimposed on the basic seven line spectra of radicals
derived from MCA the following changes in features. Line D becomes
nearly a shoulder and the resonance near $\underline{g}$ = 2 was significantly
broadened at the low field side indicating unresolved hyperfine
interactions. This is supported by three additional sharp peaks on the
high field side. Finally the high field peaks G and I had greatly
reduced intensities as compared to irradiated poly(MCA) or copolymers
of lower TCEMA contents. The additional features may be interpreted as
a radical with $\underline{g}$ = 2.0085, H_A = 14.5G and incompletely resolved ^{35}Cl
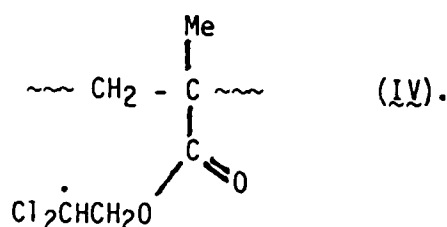hyperfine splittings. Mishra et al.[9] reported for $CCl_2\overset{\cdot}{C}H$:

$\underline{g_x}$ = 2.0023, $\underline{g_y}$ = 2.0084, $\underline{g_z}$ = 2.0100, $\underline{g}_{iso}$ = 2.0085;

$$^H\underline{A}_x = -20G, \qquad ^H\underline{A}_y = -13G, \qquad ^H\underline{A}_z = -27G, \qquad ^H\underline{A}_{iso} = -20G;$$

and $^{Cl}\underline{A}_x = +20G,$ $^{Cl}\underline{A}_y = -4G,$ $^{Cl}\underline{A}_z = -4G,$ $^{Cl}\underline{A}_{iso} = +4G.$

Since radicals in this copolymer has very nearly the same $\underline{g}_{iso}$ and $^H\underline{A}_{iso}$ values, we tentatively assign to it the structure

$$\sim\sim CH_2 - \underset{\underset{\underset{Cl_2\overset{\displaystyle .}{C}HCH_2O}{}}{\overset{\displaystyle C}{\diagdown_{\diagdown O}}}}{\overset{\overset{\displaystyle Me}{|}}{\underset{|}{C}}} \sim\sim \qquad (\underline{IV}).$$

Therefore, the irradiated poly(70MCA-co-30TCEMA) has radical $\underline{IV}$ in addition to $\underline{I}$ and $\underline{II}$. The microwave broadening of these radicals differ, decreasing in the order $\underline{II}>\underline{I}>\underline{IV}$. Figure 9b showed that at 30mW klystron power, the high field lines of radical $\underline{II}$ became very broad, the low field lines primarily due to radical $\underline{I}$ has nearly unchanged width, whereas features due to species $\underline{IV}$ became significantly sharpened.

Finally, heating of the γ-irradiated poly(70MCA-co-30TCEMA) did not convert radicals $\underline{I}$ and $\underline{II}$ to $\underline{III}$. But all three radicals decrease in concentration monotonically with the increase of temperature as shown in Figure 10. The ESR signals disappeared between 80° and 100°, well below the T_g of 136° for this copolymer.

Fig. 10

c. GC-MS.-Gamma radiolysis products were anuiyzed for poly(70MCA-co-30TFEMA) and poly(70MCA-co-30TCEMA), hereafter referred to as the fluro and chloro-copolymer, respectively. They were chosen for three reasons: they have the same MCA content, the fluro-copolymer has very high G_s = 5.5 and some crosslinking but the irradiated copolymers remain soluble after radiolysis, and the chloro-copolymer has the minimum G_s = 1.5 and maximum G_x = 0.15 for the several copolymers of TCEMA. Analysis on poly(TFEMA) was performed for reference. The results are summarized in Table III. As expected fluorine containing products were found only in the irradiated fluoro-copolymer and products containing CCl_3 and CCl_2 groups were found only in the irradiated chloro-copolymer. The HCl yields are twice as high in the chloro-copolymer. The main difference is that radiolysis caused the formation of monomer and monomer minus the CF_3 group in the fluoro-copolymer but that no monomer or monomer minus the CCl_3 group was found in the irradiated chloro-copolymer. For most of the other products they were produced in comparable amounts for both copolymers.

Table III

Table III   Volatile γ-radiolysis products

Products[a]	Poly(TFEMA)	poly(70MCA-co-30TFEMA)	poly(70MCA-co-30TCEMA)
CH_4	4.4	8.1	8.1
CO, $CH_2=CH_2$	14.2	0.6	0.6
C_2H_6, HCO^+	11.0	2.5	2.5
CH_3OH	2.0	0.6	0.6
CH_3F	1.2	1.0	
$H^{35}Cl$	-	36.7	85.7
$H^{37}Cl$	-	16.9	39.3
C_3H_6	152.3	3.4	3.3
CO_2	100	100	100
C_2H_3F	4.1	14.4	-
$CH_3{}^{35}Cl$	-	106	112.6
$CH_3{}^{37}Cl$	-	33.3	38
$HCOOCH_3$	3.1	7.2	3.9
$CH_3CH_2{}^{35}Cl$		5.2	2.2
$CH_3CH(F)OH$	7.9		
$CH^3CH_2{}^{37}Cl$	-	1.0	1.0
$CH_2=C(Me)CO^+$	79.7	43.9	0.7
CHF_3	97	45	-
CF_3CH_3	3.3	3.2	-
CF_3OH	5.6	-	-
$CH_2=C(Me)COOCH_2{}^+$	0.9	0.8	-
CH_2Cl_2 (all isotopes)	-	-	2.9
$CHCl_3$ (all isotopes)	-	-	1.1
$CH_2=C(Me)COOCH_2CF_3$	2.6	3.2	-

[a]Relative ion current normalized to 100 for CO_2

The major difference in the radiolysis products of the homo- and co-polymer of TFEMA is that the former has large yields of hydrocarbons whereas they are much smaller in the copolymer due to formation of alkylchlorides in the presence of MCA monomer.

Mechanism. - We note first that with certain compositions the copolymers have G_S greater than homopolytrihaloethylmethacrylate and G_X = 0. Therefore, poly(38MCA-co-62TFEMA) is better than the poly(TFEMA) and has G_S value 2.3 times larger than PMMA. Poly(94MCA-co-6TCEMA) has G_S = 2.7 and G_X = 0. The truly remarkable point is that with only 6 mole % of TCEMA, the tendency of poly(MCA) to crosslink was completely suppressed.
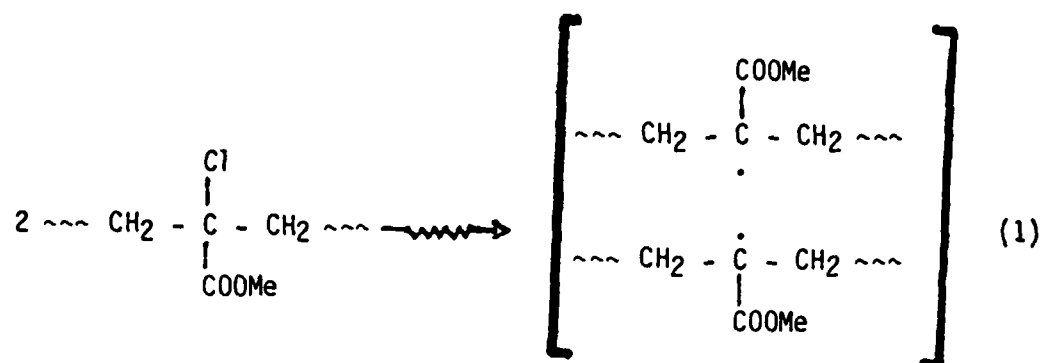
Before discussing the copolymer radiolysis, we should realize that both poly(TFEMA) and poly(TCEMA) with G_S values of 2.0 and 2.4, respectively, and G_X = 0 are promising resists. The radiolysis mechanism of poly(TCEMA) have already been discussed.[3] The similarities of radiolysis yields, ESR spectra and volatile product analysis suggest that the mechanism also applies to poly(TFEMA). Since the primary process is believed to be dissociative electron capture, the results imply chlorine atoms have larger cross section for this process than the fluorine atoms.

The absence of crosslinking in poly(TFEMA) and poly(TCEMA) is supported by the ESR results that only terminal radicals of type IV were observed. Combination of two such radicals would result only in chain
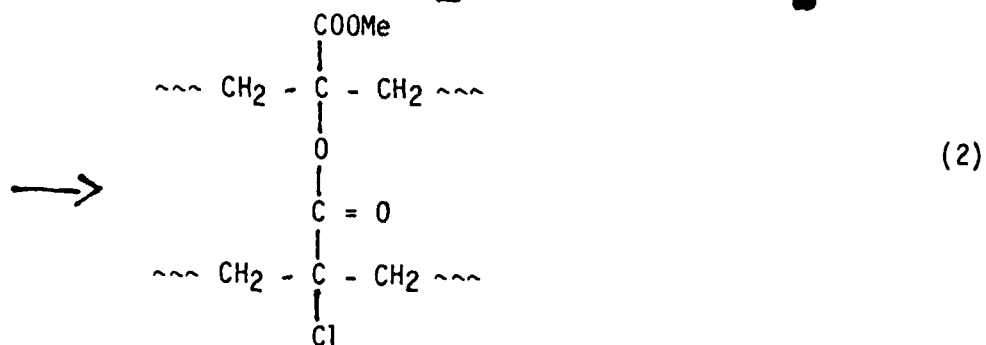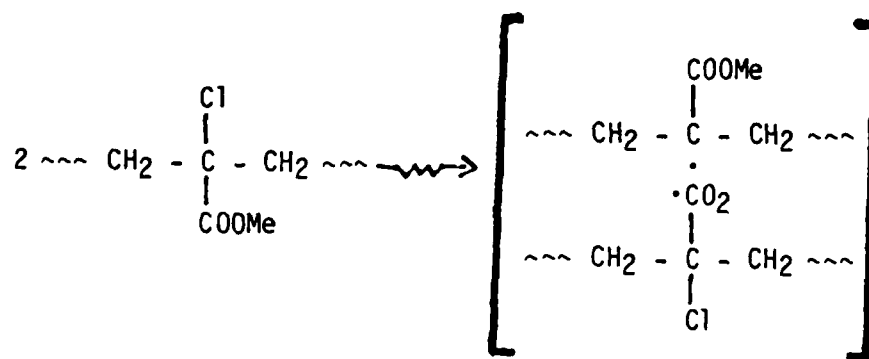
extension. Even if it reacts with a main chain radical only a long branching is formed. Crosslinking would require further reactions of the main chains of the branched macromolecule. To wit, radiolysis of PMMA produces only type $\underset{\sim}{IV}$ radicals. One may argue that during room temperature irradiation that some of the radicals may have already recombined and were not seen by ESR. This is probably true, even under these conditions $G_{\underline{r}}$ values are usually greater than $G_{\underline{s}} + G_{\underline{x}}$. The volatile products of polymers irradiated at low temperatures and ESR recorded at low temperatures would be quite different from the room temperature results. We believe the room temperature experiments are more relevant than low temperature ones because electron or x-ray lithography are usually done at ambient temperatures. In so far as the crosslinking processes are concerned they require the involvement of main chain radicals whose motion is possible only in the vicinity of T_g.

The radiolysis mechanism of poly(MCA) has been described earlier.[2] Its tendency toward crosslinking may be attributed to the efficient dissociative electron capture by the α-chlorine atoms to produce main chain radical $\underset{\sim}{II}$. Though radical $\underset{\sim}{II}$ is known to undergo dissociative rearrangement for form radical $\underset{\sim}{I}$, the process is incomplete and both radicals were seen by ESR.

Some polymers such as poly(2-fluoroethylmethacylate),[3] poly(MCA),[2] and poly(TFEMA) of this work showed a significant fraction of the radicals to recombine slightly above ambient temperature, i.e. well below the T_g. We have attributed this to geminal recombination. It is well known in the interaction of γ-ray with matter that the Compton process produces spurs of low energy electrons. If there are atoms with high capture cross section such as in these halogenated homopolymers, there will be produced radicals in close proximity. Germinal recombination would result when the molecules assume additional rotation or chain twisting. These processes would be undesirable from the standpoint of lithographic application. Recombination of terminal radicals would increase molecular weight and decreases the effective $\underline{G_s}$. Reactions between main chain radicals would increase the effective $\underline{G_x}$. In the case of poly(MCA) the spur effect may lead to crosslinking by reactions such as:
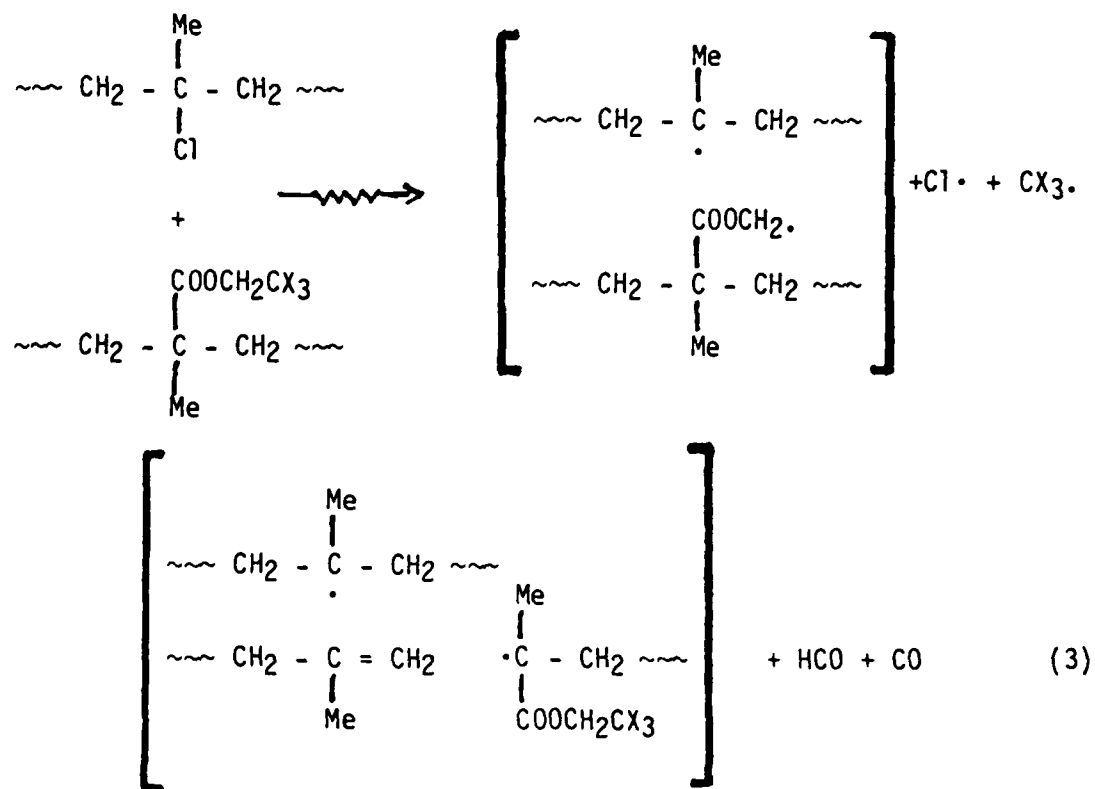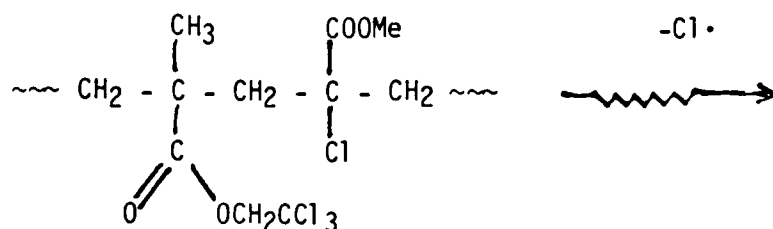
$$2 \sim\sim CH_2 - \underset{\underset{COOMe}{|}}{\overset{\overset{Cl}{|}}{C}} - CH_2 \sim\sim \longrightarrow \left[\begin{array}{c} \sim\sim CH_2 - \underset{\underset{\bullet}{|}}{\overset{\overset{COOMe}{|}}{C}} - CH_2 \sim\sim \\ \\ \sim\sim CH_2 - \underset{\underset{COOMe}{|}}{\overset{\overset{\bullet}{|}}{C}} - CH_2 \sim\sim \end{array} \right] \qquad (1)$$

$$\longrightarrow \quad \begin{array}{c} \sim\sim CH_2 - \underset{|}{\overset{\overset{COOMe}{|}}{C}} - CH_2 \sim\sim \\ \sim\sim CH_2 - \underset{\underset{COOMe}{|}}{\overset{|}{C}} - CH_2 \sim\sim \end{array}$$

or

$$2 \sim\sim CH_2 - \underset{\underset{COOMe}{|}}{\overset{\overset{Cl}{|}}{C}} - CH_2 \sim\sim \longrightarrow \left[\begin{array}{c} \sim\sim CH_2 - \underset{\underset{\bullet CO_2}{|}}{\overset{\overset{COOMe}{|}}{C}} - CH_2 \sim\sim \\ \\ \sim\sim CH_2 - \underset{\underset{Cl}{|}}{\overset{|}{C}} - CH_2 \sim\sim \end{array} \right]$$

$$\longrightarrow \quad \begin{array}{c} \sim\sim CH_2 - \underset{\underset{\underset{\underset{\underset{Cl}{|}}{\sim\sim CH_2 - C - CH_2 \sim\sim}}{C = 0}}{O}}{\overset{\overset{COOMe}{|}}{C}} - CH_2 \sim\sim \end{array} \qquad (2)$$
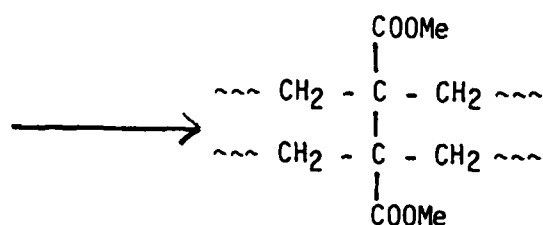
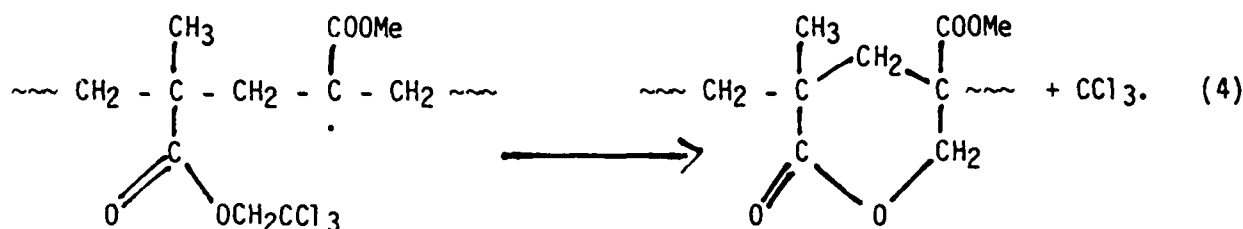According to this reasoning the effect of MMA on $G_{\underline{x}}$ in its copolymer with MCA may be rationalized.

The copolymers of MCA with trihaloethylmethacylates have reduced crosslinking tendencies even though the densities of halogen atoms are greater than in poly(MCA). This may be explained by the fact that terminal radicals of type $\underline{III}$ are produced in the radiolysis of TCEMA and TFEMA units. Also the transformation of one of the primary radials may also promote the separation of radical pairs produced initially in close proximity. For the purpose of illustration we write

$$
\begin{array}{c}
\text{Me} \\
| \\
\sim\!\sim CH_2 - C - CH_2 \sim\!\sim \\
| \\
Cl \\
+ \\
COOCH_2CX_3 \\
| \\
\sim\!\sim CH_2 - C - CH_2 \sim\!\sim \\
| \\
Me
\end{array}
\xrightarrow{\text{\scriptsize$\sim\!\sim\!\sim$}}
\left[
\begin{array}{c}
\text{Me} \\
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\cdot \\
\\
COOCH_2\cdot \\
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\sim\!\sim CH_2 - C - CH_2 \sim\!\sim \\
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Me
\end{array}
\right]
+ Cl\cdot + CX_3\cdot
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$$
\left[
\begin{array}{c}
\text{Me} \\
| \\
\sim\!\sim CH_2 - C - CH_2 \sim\!\sim \\
\cdot \qquad\qquad\qquad \text{Me} \\
\qquad\qquad\qquad\qquad | \\
\sim\!\sim CH_2 - C = CH_2 \qquad \cdot C - CH_2 \sim\!\sim \\
| \qquad\qquad\qquad\qquad | \\
Me \qquad\qquad\qquad COOCH_2CX_3
\end{array}
\right]
+ HCO + CO \qquad\qquad (3)
$$

In the previous studies of MMA copolymers with methyl-α-haloacrylates[2] and haloalkylmethacrylates,[3] it was shown that the primary radiolysis is controlled by the dissociative electron capture by the halogenated monomers. In this work, the processes occur for both comonomers. This is evidenced by the formation of radicals of type I, II and III in the radiolysis of MCA-TFEMA copolymers. The results of Figure 7 suggests that radical I is transformed to II and/or III. Several possible pathways can be postulated for these conversions, but present data do not justify the speculation.

Radiolysis of poly(94MCA-co-6TCEMA) has several interesting points. Only type I and II radicals were observd by ESR but not the type III radicals even after heating the irradiated copolymer. This may be rationalized by the low TCEMA contents which is the source of PMMA type radical III. The unexpected behaviors are that with only 6 mole % of TCEMA G_x becomes zero and there are no evidence of geminal radical recombination as the copolymer was slightly heated. It may be proposed that at low TCEMA content electrons are captured mostly by the α-chlorine atoms of MCA and an intramolecular cyclization occurs to eliminate the stable $CCl_3\cdot$ radical.

$$\sim\sim CH_2 - \underset{\underset{\displaystyle O\diagdown \quad OCH_2CCl_3}{\overset{\displaystyle \|}{C}}}{\overset{\displaystyle CH_3}{\underset{\displaystyle |}{\overset{\displaystyle |}{C}}}} - CH_2 - \underset{\underset{\displaystyle Cl}{|}}{\overset{\displaystyle COOMe}{\overset{\displaystyle |}{C}}} - CH_2 \sim\sim \qquad \overset{\displaystyle -Cl\cdot}{\xrightarrow{\hspace{2cm}}}$$

$$\sim\!\!\sim CH_2 - \underset{\underset{\underset{\underset{OCH_2CCl_3}{\overset{\displaystyle O}{\diagdown}}}{\overset{\displaystyle \parallel}{C}}}{\underset{\displaystyle |}{\overset{\displaystyle CH_3}{C}}} - CH_2 - \underset{\displaystyle \bullet}{\overset{\overset{\displaystyle COOMe}{\displaystyle |}}{C}} - CH_2 \sim\!\!\sim \quad \longrightarrow \quad \sim\!\!\sim CH_2 - \underset{\underset{\diagdown}{\overset{\displaystyle O}{\underset{O}{\parallel}}}}{\overset{\displaystyle CH_3}{C}} \overset{CH_2}{\diagup}\underset{CH_2}{\overset{COOMe}{C}}\sim\!\!\sim \; + \; CCl_3. \quad (4)$$

This process is replaced by others when electron is captured by the chlorine atoms of the pendant ester group as the TCEMA content in the polymer increases. Though why the effectiveness is highest at very low TCEMA content is not clear. However, in the reported radiolysis of copolymers it is not uncommon to find that G_s and/or G_x attains minimum or maximum values at certain composition with low percentage of one of the monomers. Consequently, any search for resist copolymers must include the entire range of composition preferably at five percent intervals.

In contrast to the TCEMA copolymers, the radiolysis yields of TFEMA copolymers vary monotonically with composition. The different behaviors may be due to the fact that the TFEMA copolymers have a tendency to depolymerize but not the TCEMA copolymers. Table III showed the formation of $CH_2=C(Me)COOCH_2CF_3$ and $CH_2=C(Me)COOCH_2^+$ from the fluoro-copolymers but similar products were not detected in the irradiated chloro-copolymer sample. Therefore, the former has much

lower tendency for scission. One of the reason may be reaction leading to the relatively stable radical $\underset{\sim\sim}{IV}$ which is of some stability.

In conclusion this radiolysis study showed the importance of investigating a broad range of copolymer composition. Four non-crosslinking systems were found to be potential positive resists arranged in increasing order of promise are: poly(TFEMA), poly(TCEMA), poly(94MCA-co-6TCEMA) and poly(68MCA-co-32TFEMA) taking into considerations G_s, G_x, and T_g. However, the actual sensitivity and contrast for lithography will depend on other considerations such as differential solubilities, dry etchability, etc. Lair et al.[10] had studied the methacrylonitrile-TCEMA system and found it to be potentially useful as etch mask for submicron structure fabrication.

Acknowledgement:

References and Notes

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Figure Captions.

Figure 1. Copolymer composition versus comonomer feed of MCA and
TFEMA: (0) experimental values; (____) curve calculated
from copolymerization equation.

Figure 2. Copolymer composition versus comonomer feed of MCA and
TCEMA: (0) experimental values; (____) curve calculated
from copolymerization equation.

Figure 3. Plots of $\overline{M}^{-1}$ of MCA-TFEMA copolymers versus D:
(a) poly(70MCA-co-30TCEMA); (b) poly(66MCA-co-34TFEMA);
(c) poly(38MCA-co-62TFEMA); (d) poly(TFEMA). (0) $\overline{M}_r^{-1}$;
(●) $\overline{M}_w^{-1}$ and lines are least square fits.

Figure 4. Plots of $\overline{M}^{-1}$ of MCA-TCEMA copolymers versus D:
(a) poly(94MCA-co-6TCEMA); (b) poly(78MCA-co-22TCEMA);
(c) poly(70MCA-co-3-TCEMA). (0) $\overline{M}_r^{-1}$; (●) $\overline{M}_w^{-1}$, and lines
are least square fits.

Figure 5. ESR spectra of γ-irradiated polymers: (a) poly(TFEMA), D =
0.69Mrad,G_r = 3.2; (b) poly(70MCA-co-30TFEMA), D = 0.9
Mrad, G_r = 7.4.

Figure 6. Microwave saturation characteristics: (a) poly(TFEMA)
(b) poly(70MCA-co-30TFEMA). The alphabets correspond to the
lines indicated in Figure 5.

Figure 7.   Variation of ESR peak intensities with temperature (a)
            poly(TFEMA); (b) poly(70MCA-co-30TFEMA). The alphabets
            correspond to the lines indicated in Figure 5.

Figure 8.   ESR spectra of γ-irradiated poly(78MCA-co-22TCEMA),
            D=3.94Mrad, G_r = 4.8, (a) 25°, 1.5mW; (b) 50°, 1.0mW;
            (c) 70°, 1.0mW; (d) 90°, 1.0mW.

Figure 9.   ESR spectra of γ-irradiated poly(70MCA-co-30TCEMA) D = 3.9
            Mrad, G_r = 5.4.   (a) 25° 1.0mW; (b) 25°, 30mW.

Figure 10. Variation of ESR peak intensities with temperature for
            poly(70MCA-co-30TCEMA). The alphabets correspond to the
            lines indicated in Figure 9a.
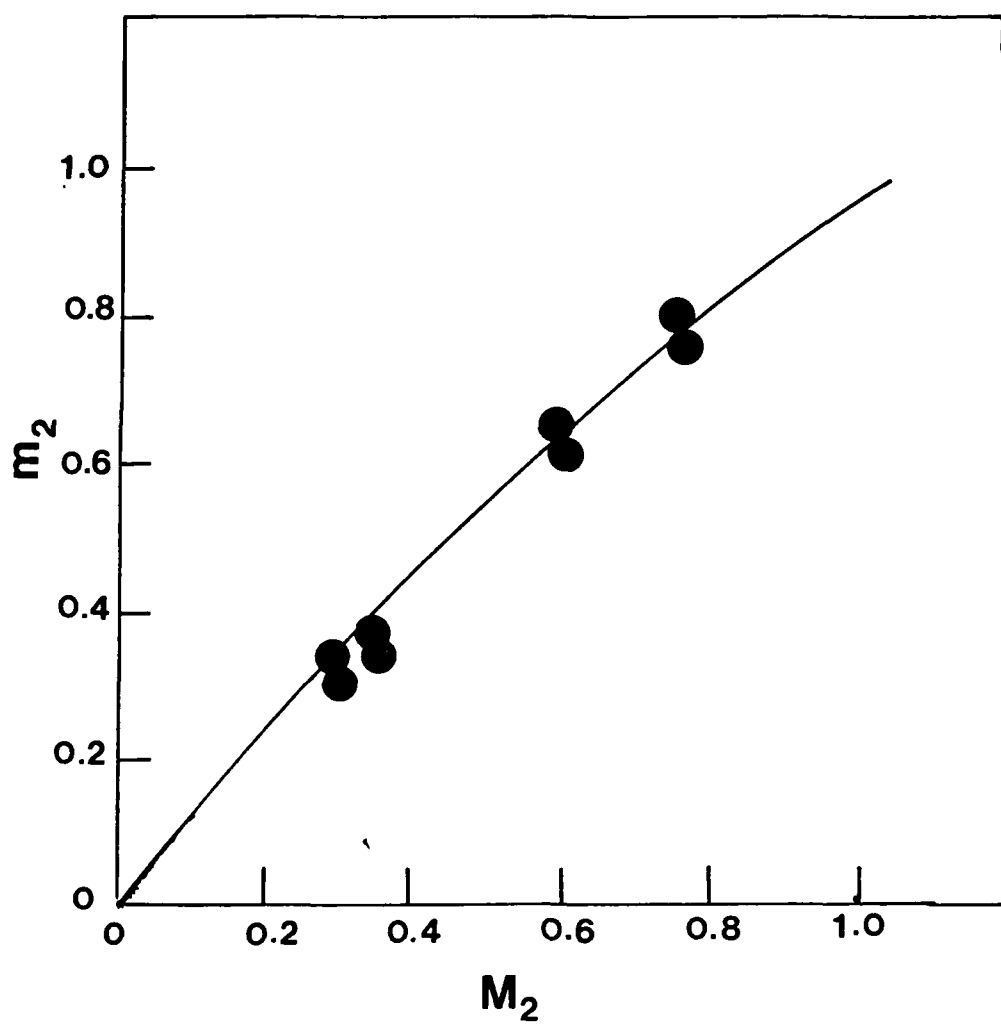
Fig.1
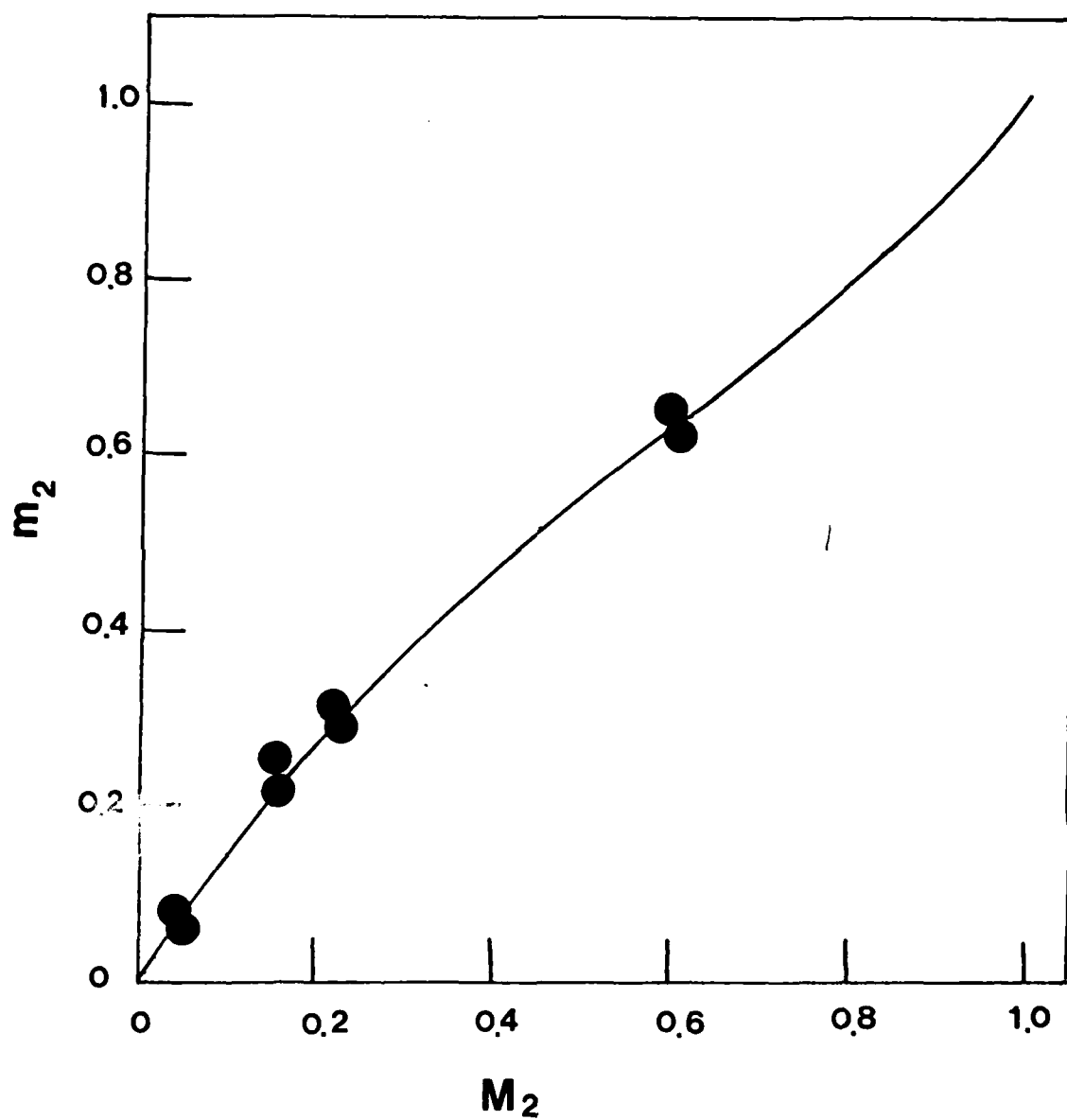
Fig. 2
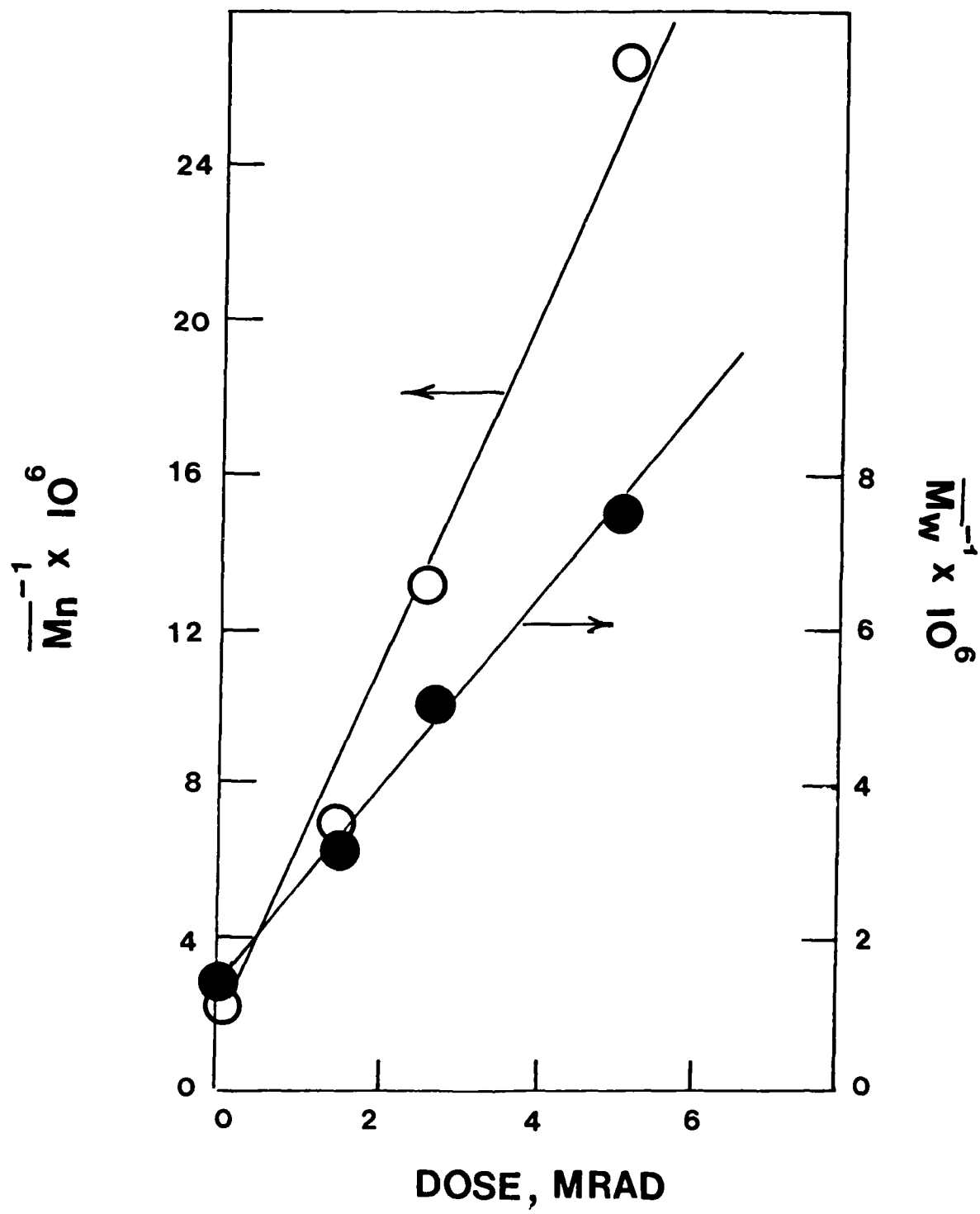
Fig.3a
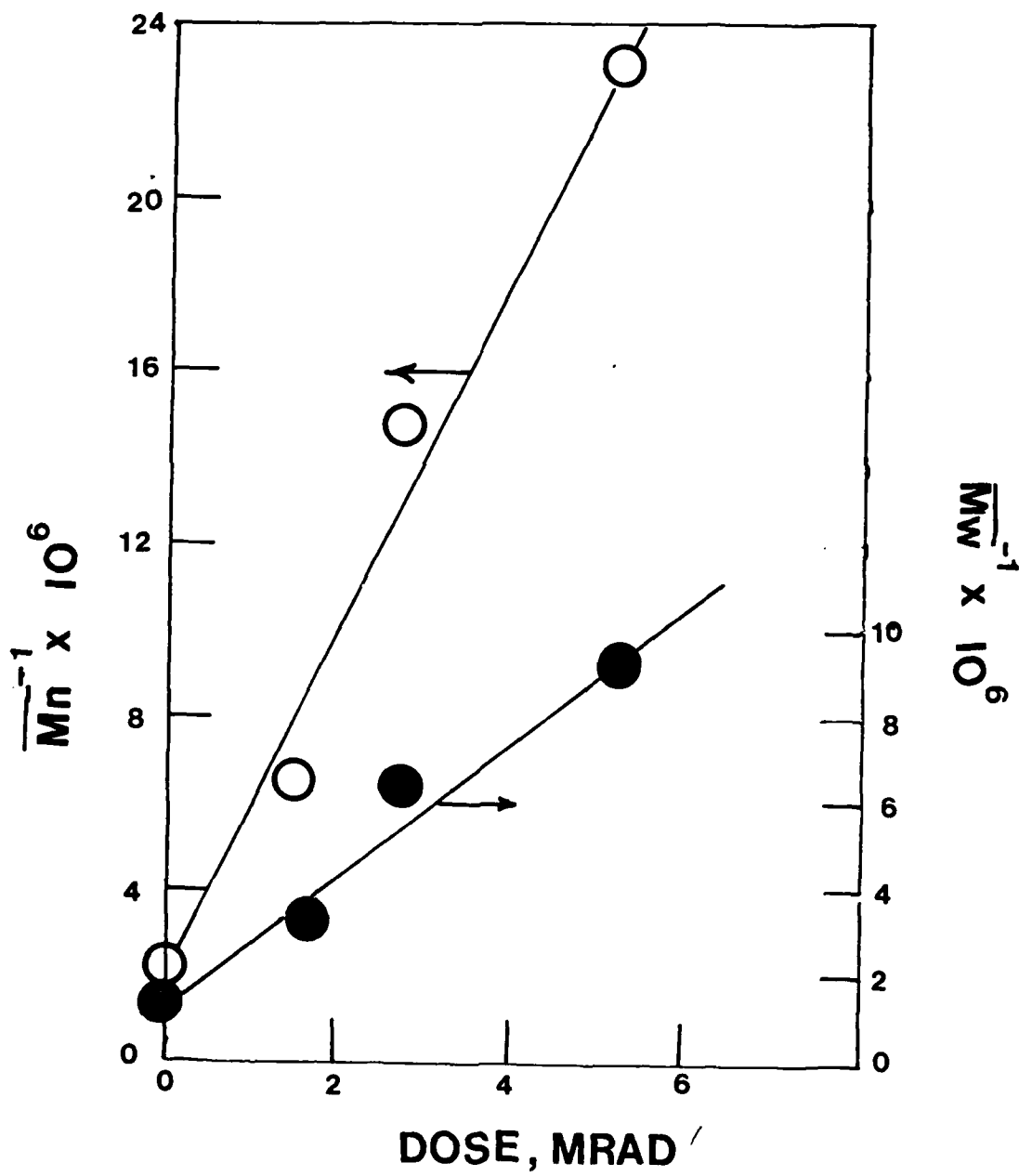
Fig.3b
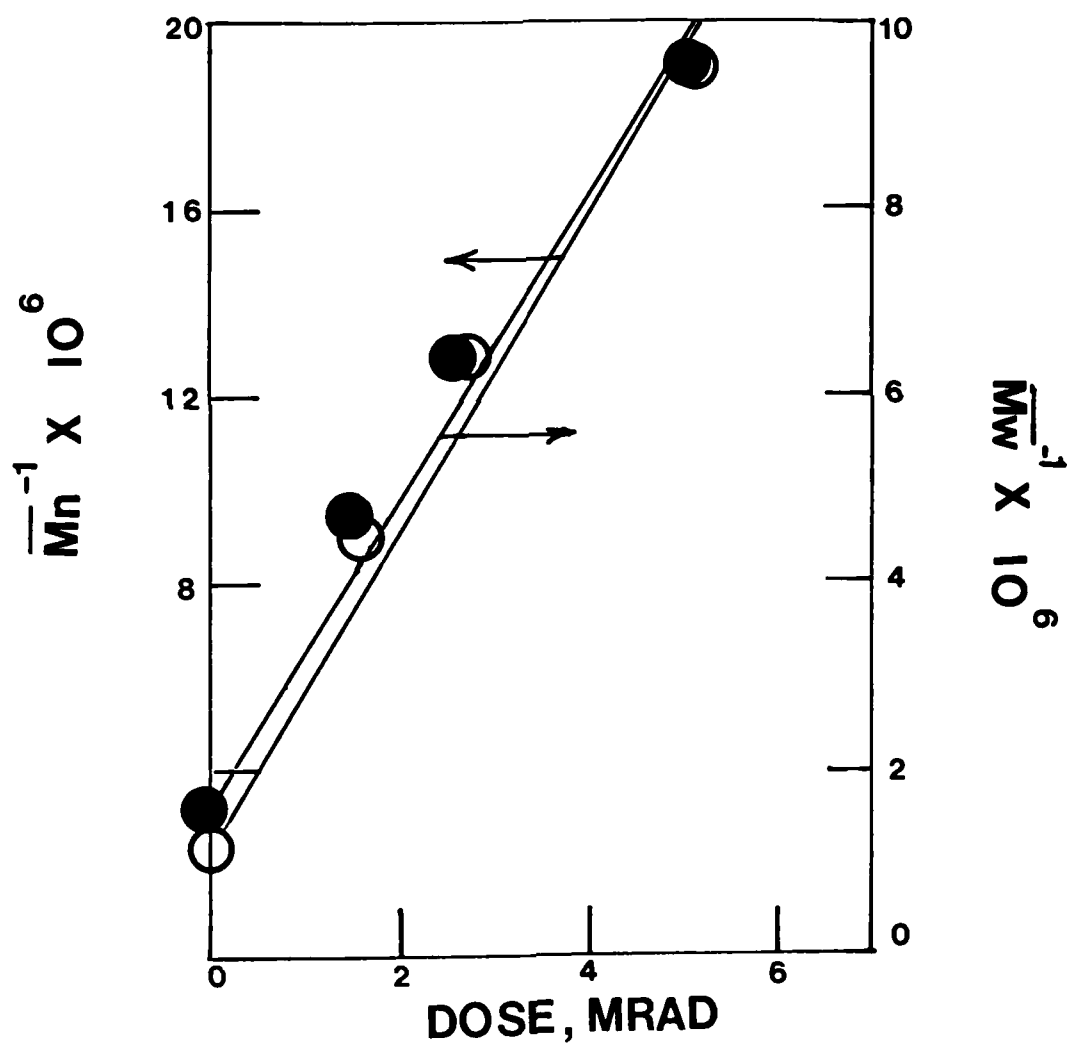
Fig.3c
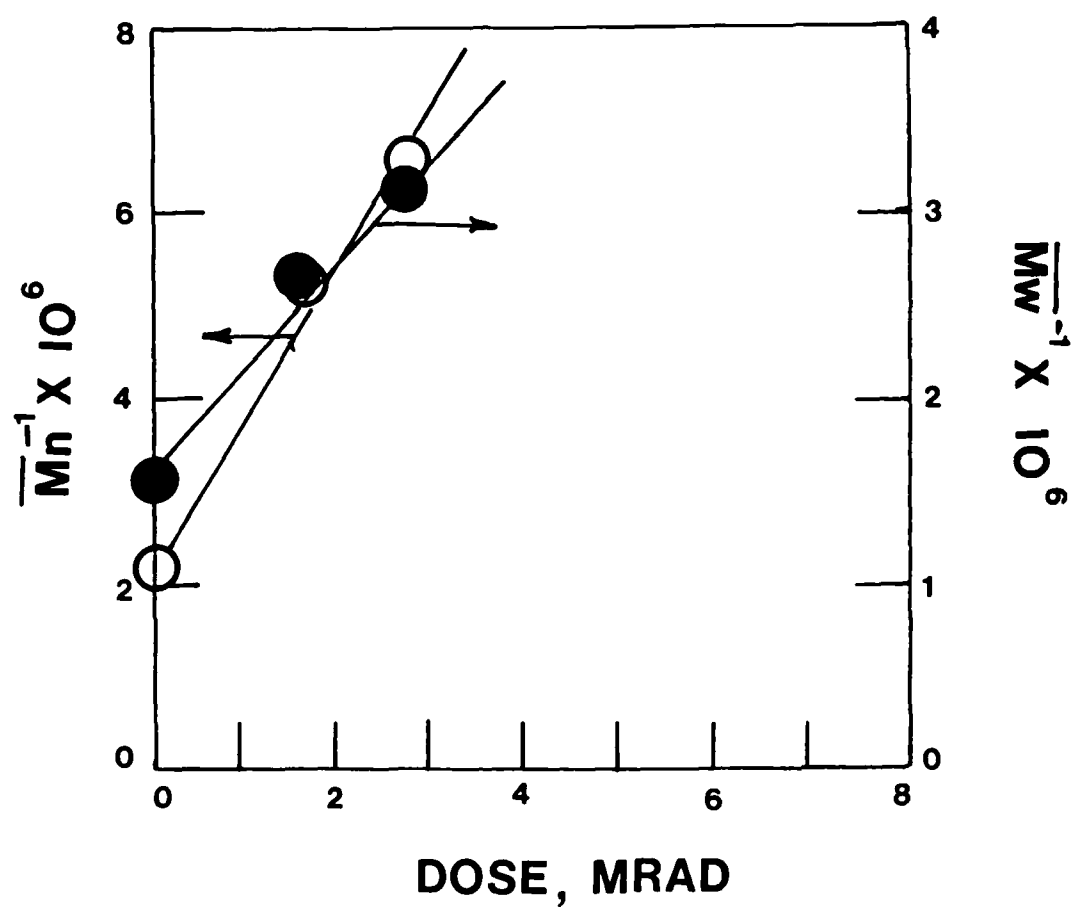
Fig.3d
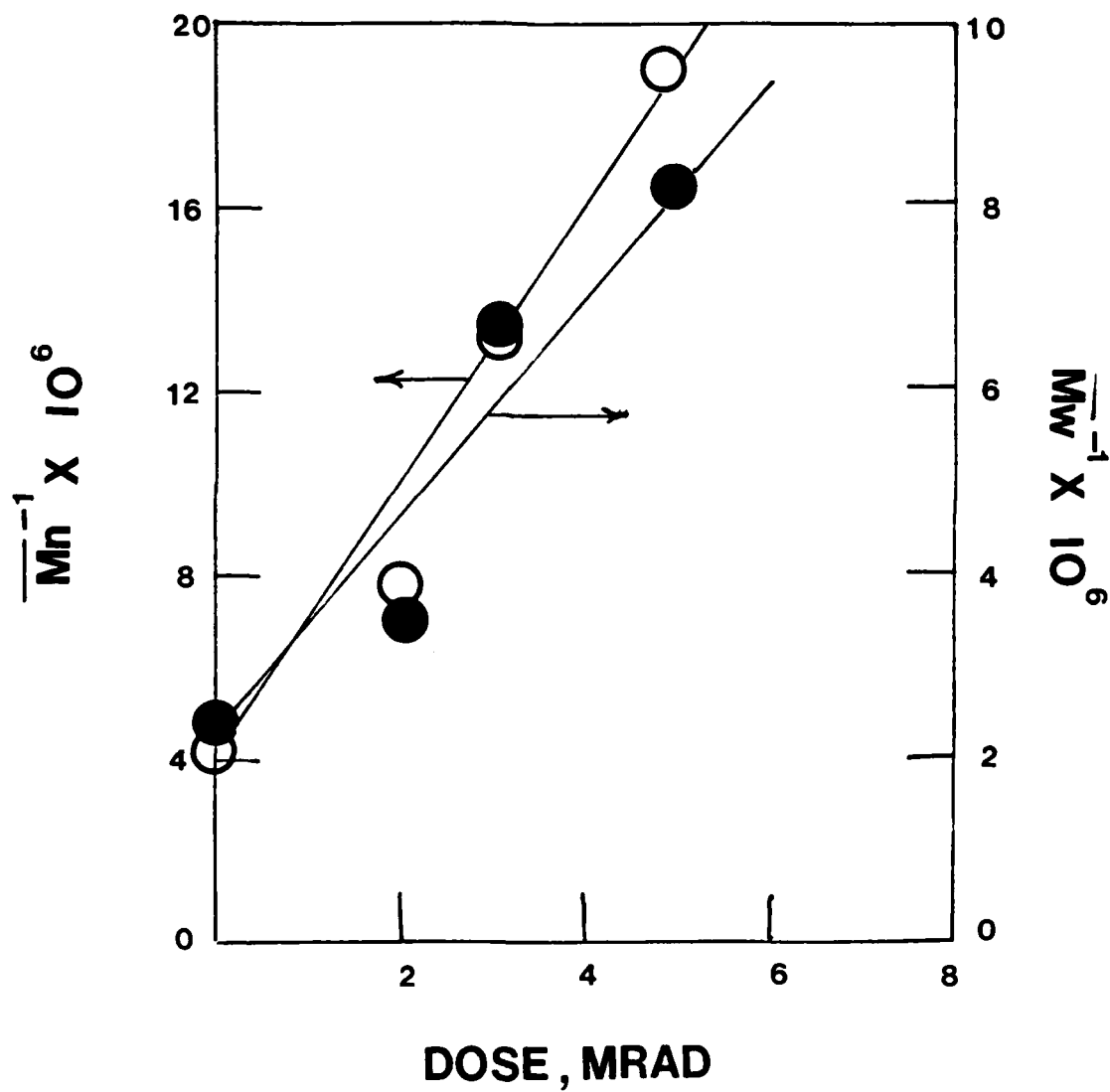
Fig. 4a

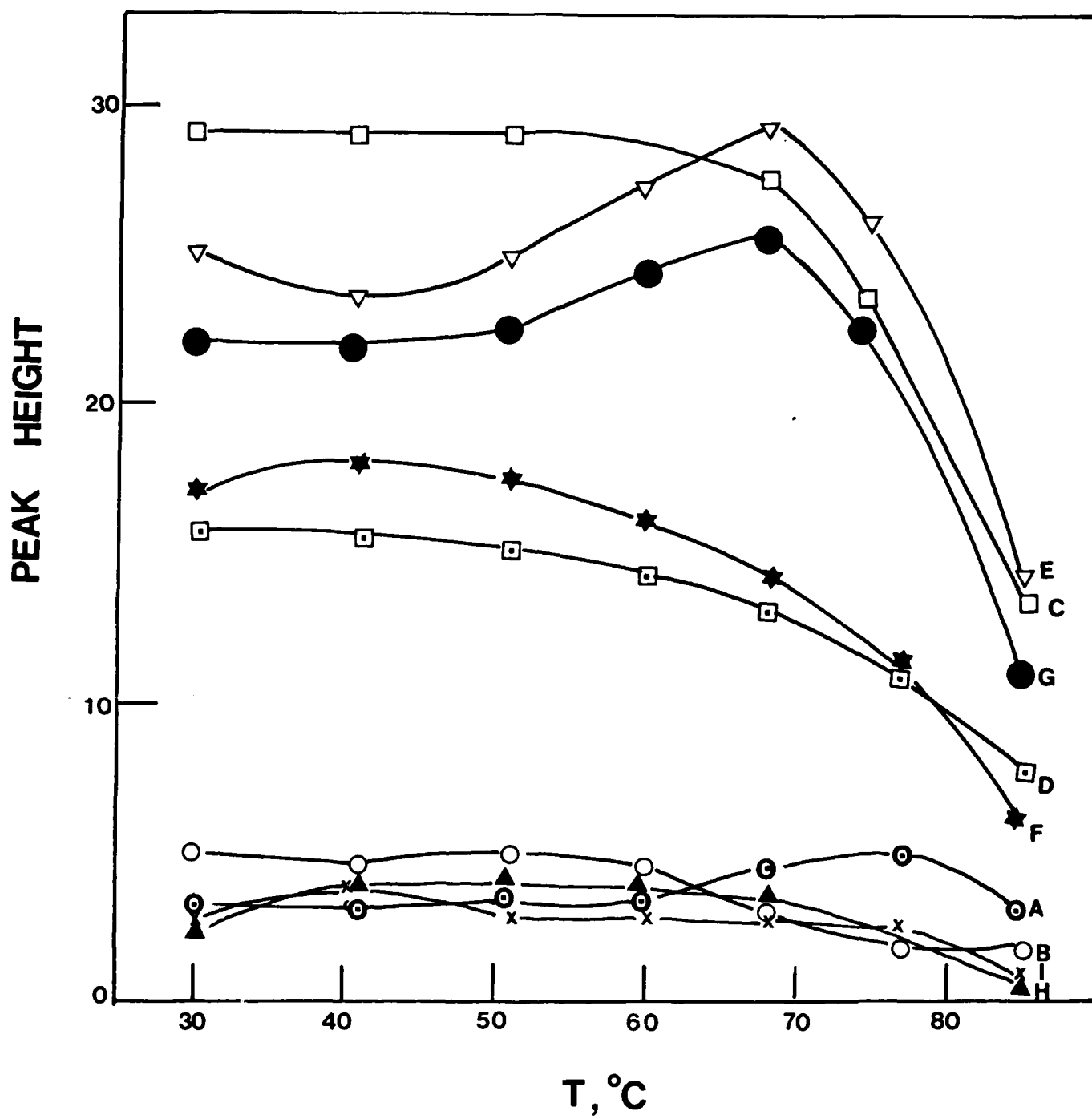Fig.4b

Fig. 4c

Fig.5a

Fig. 5b

RT

40°C

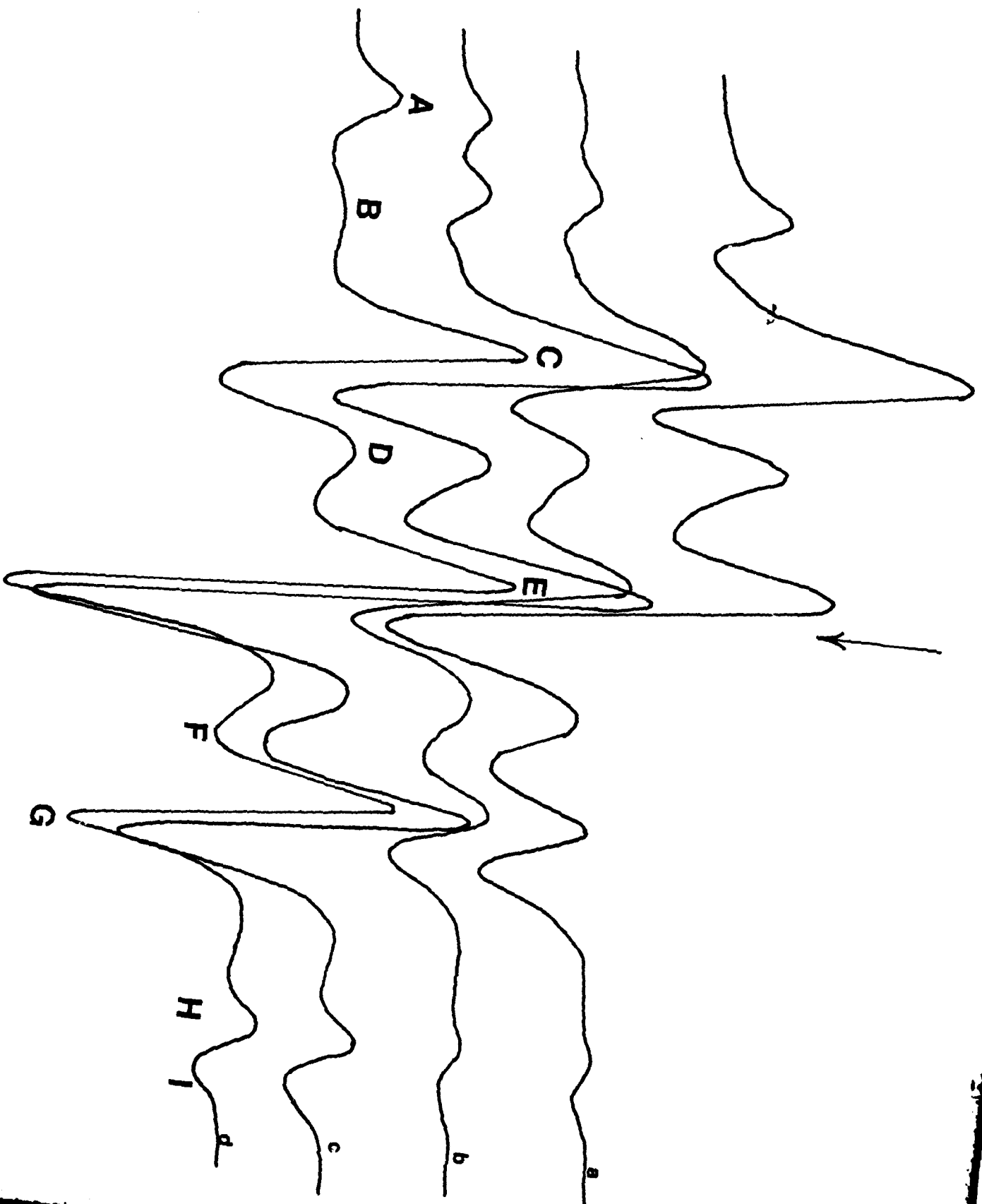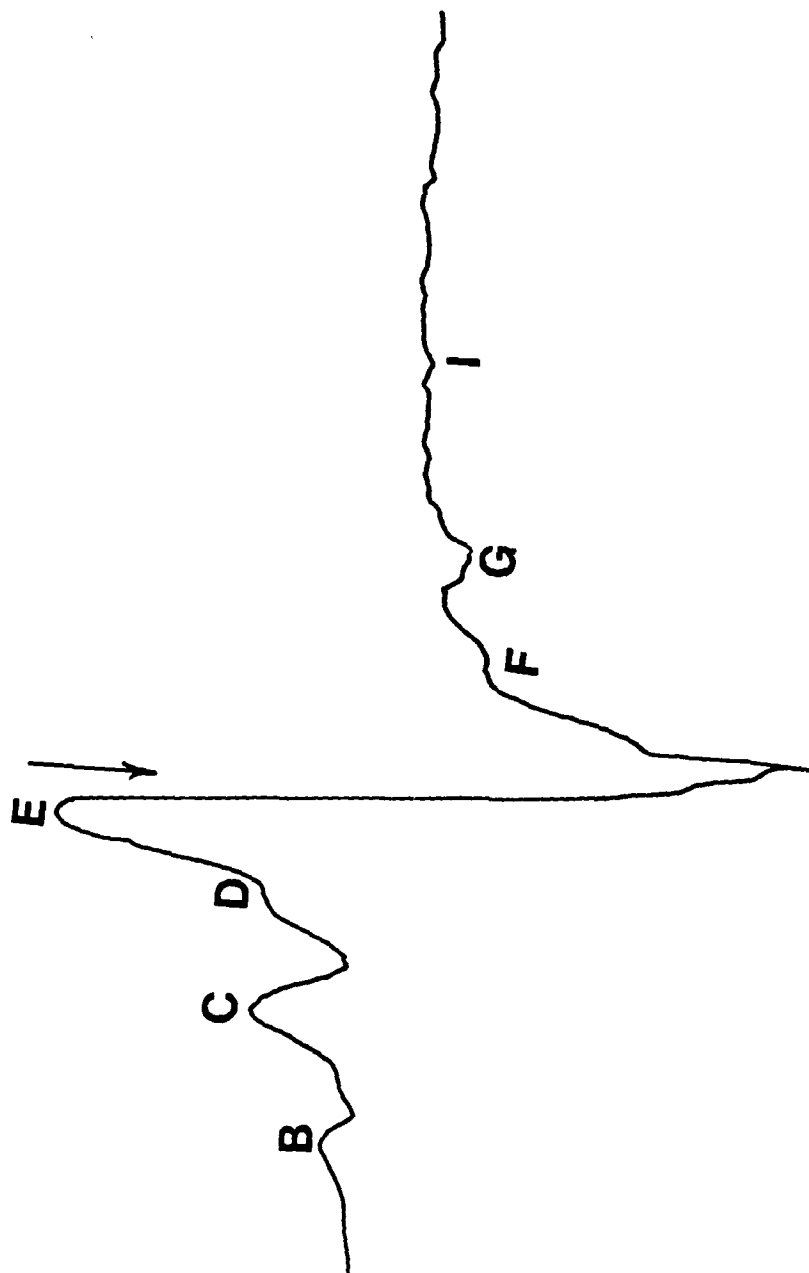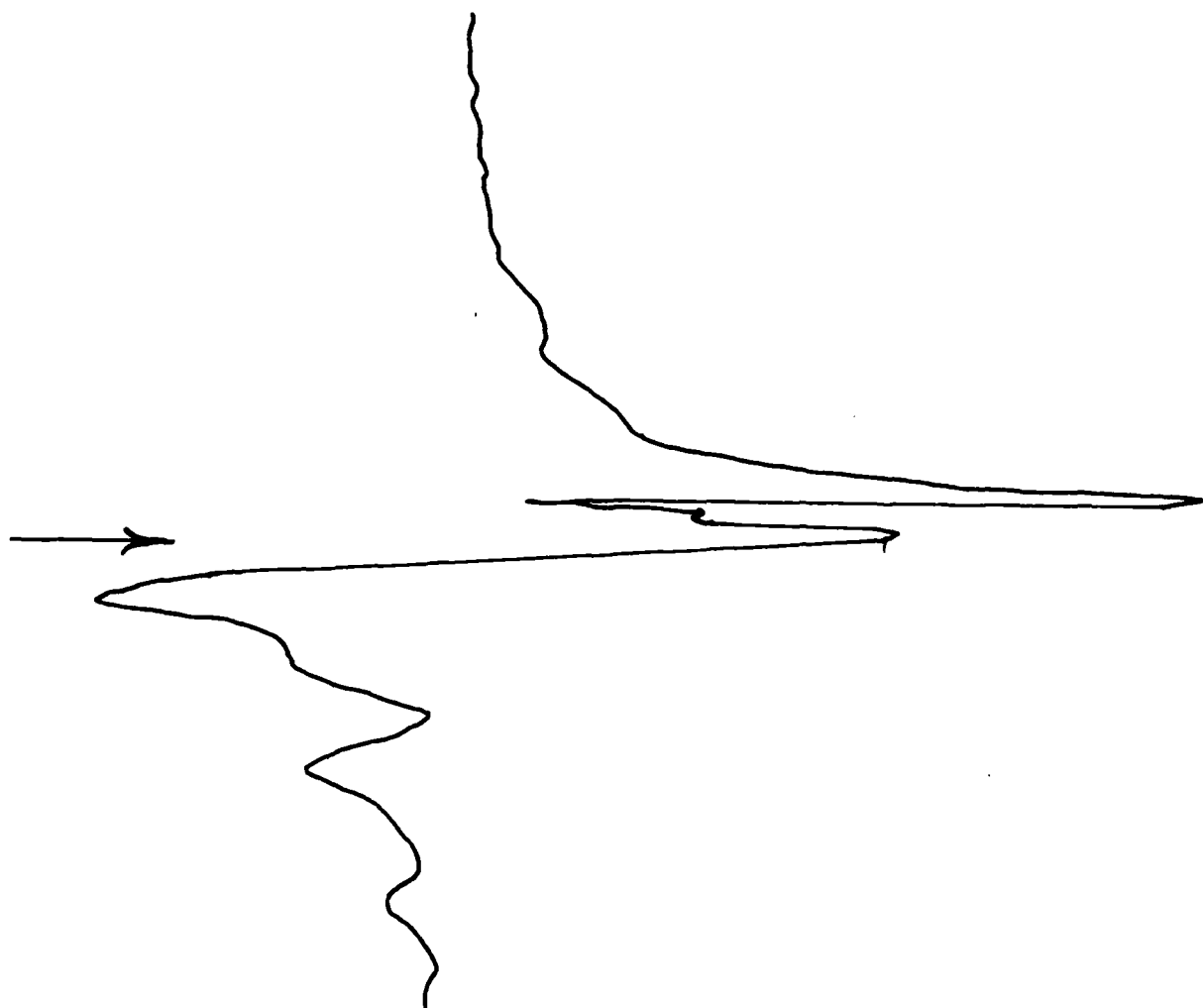50°C

60°C

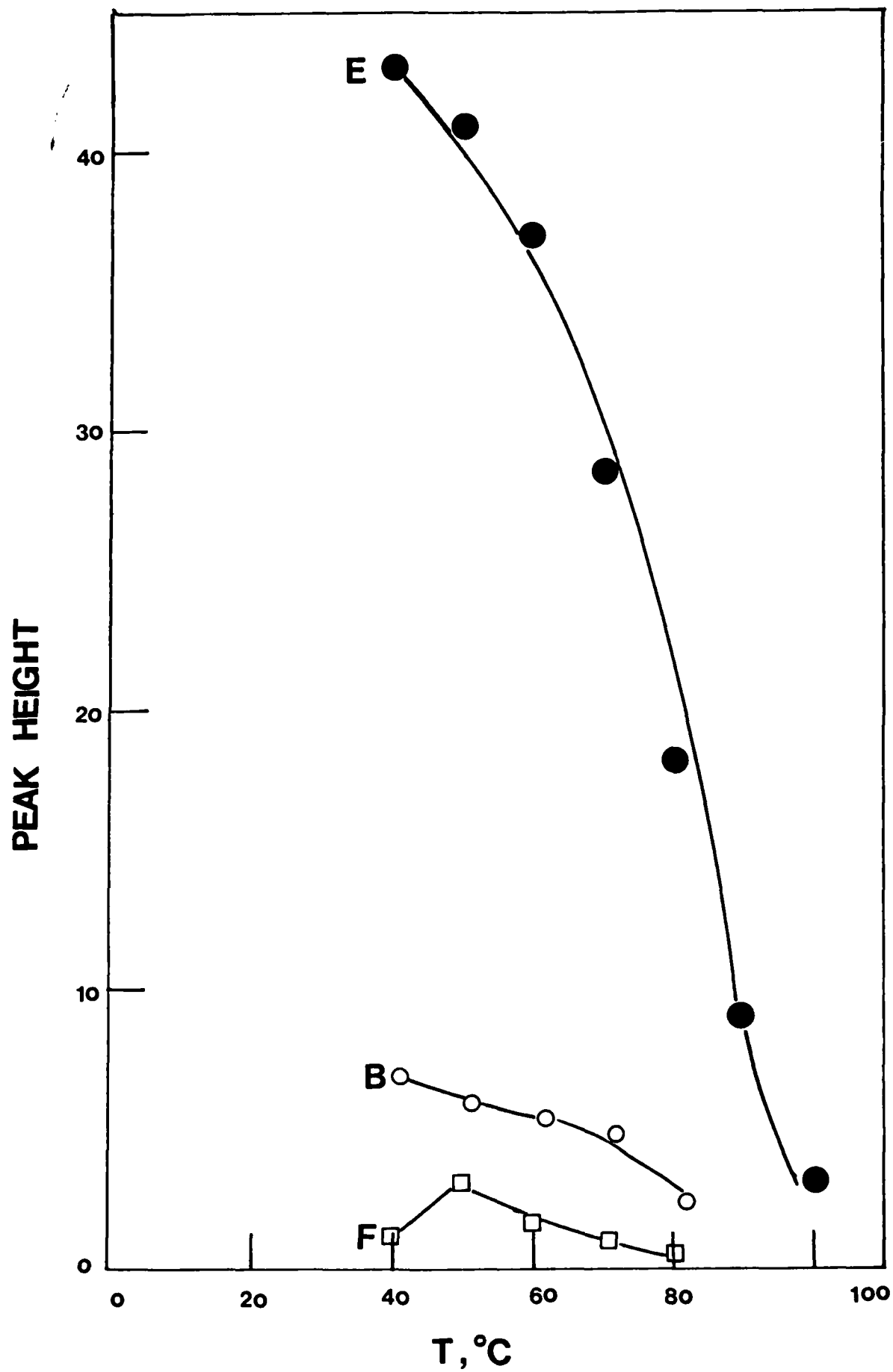70°C

80°C

20G

Fig.6a

PEAK HEIGHT
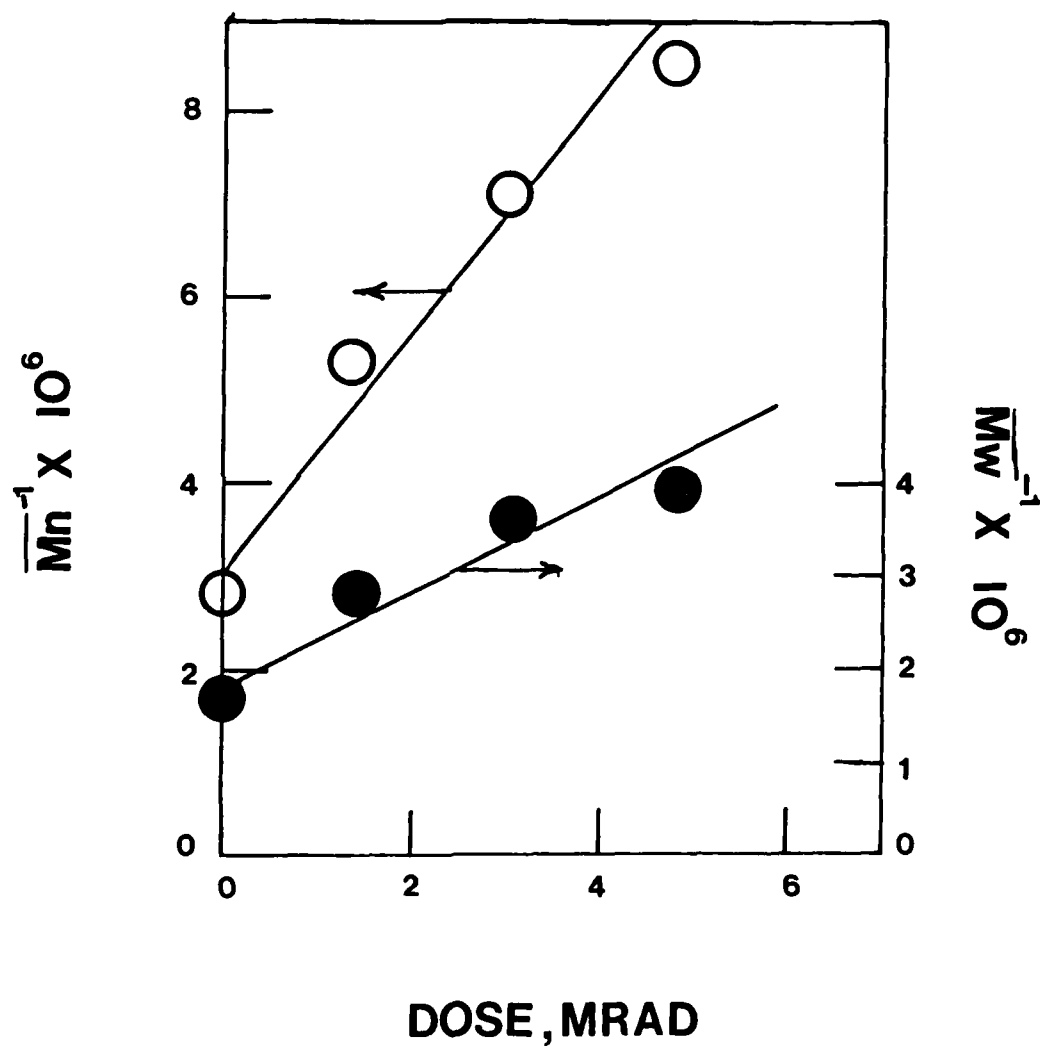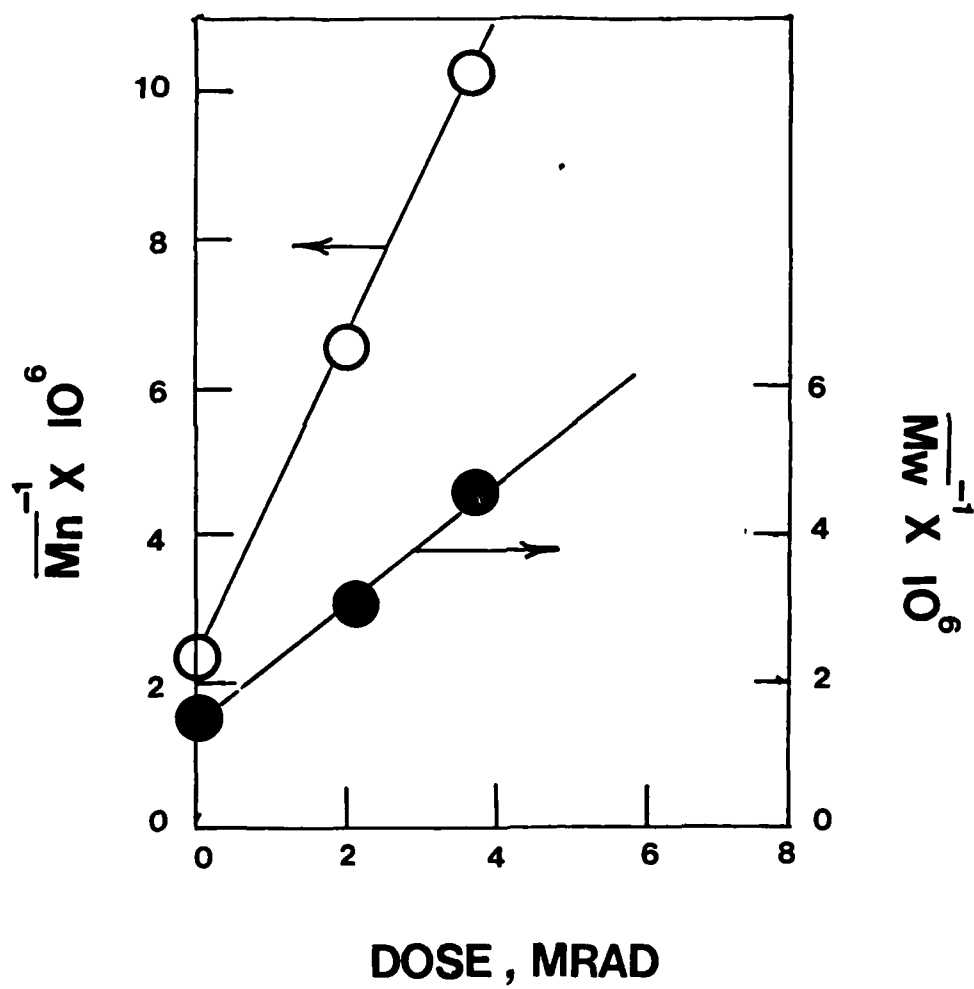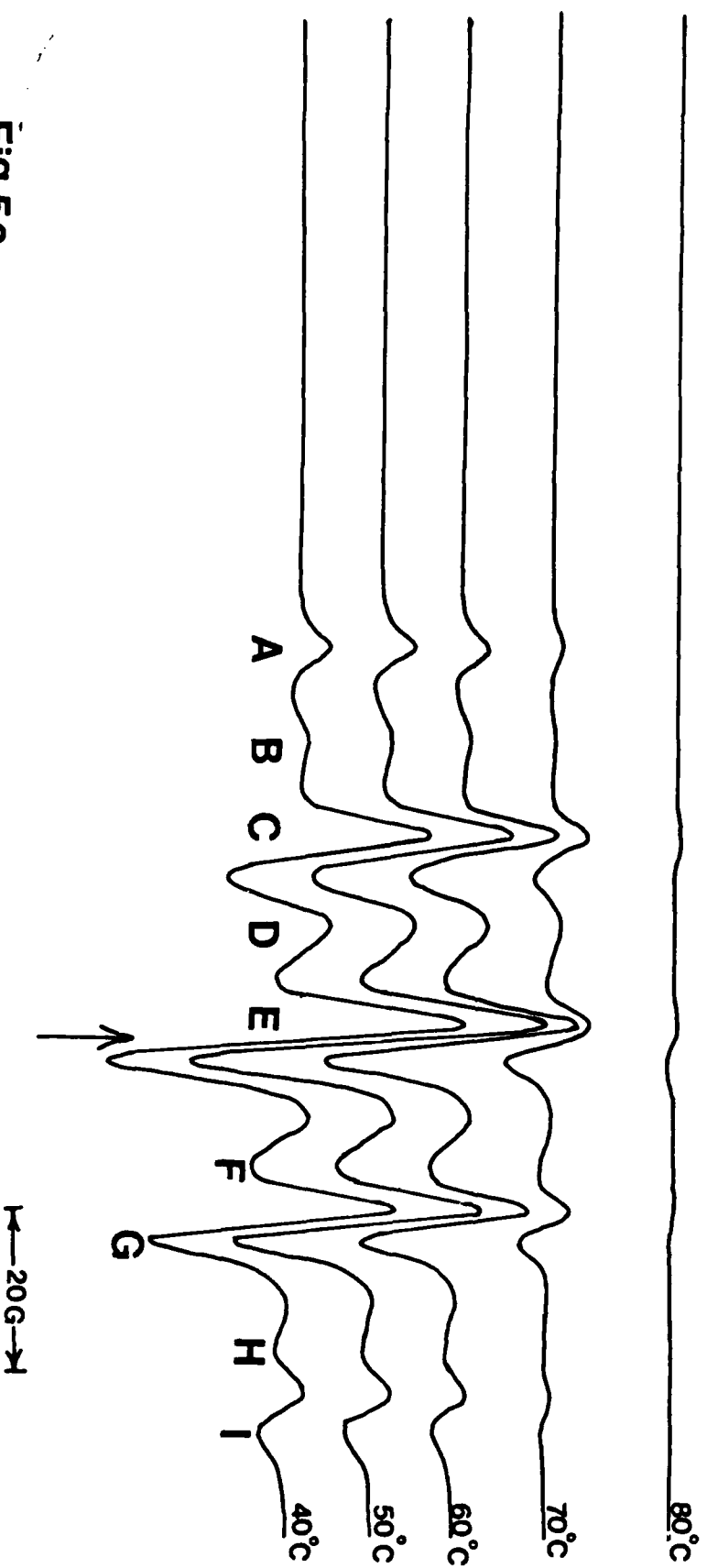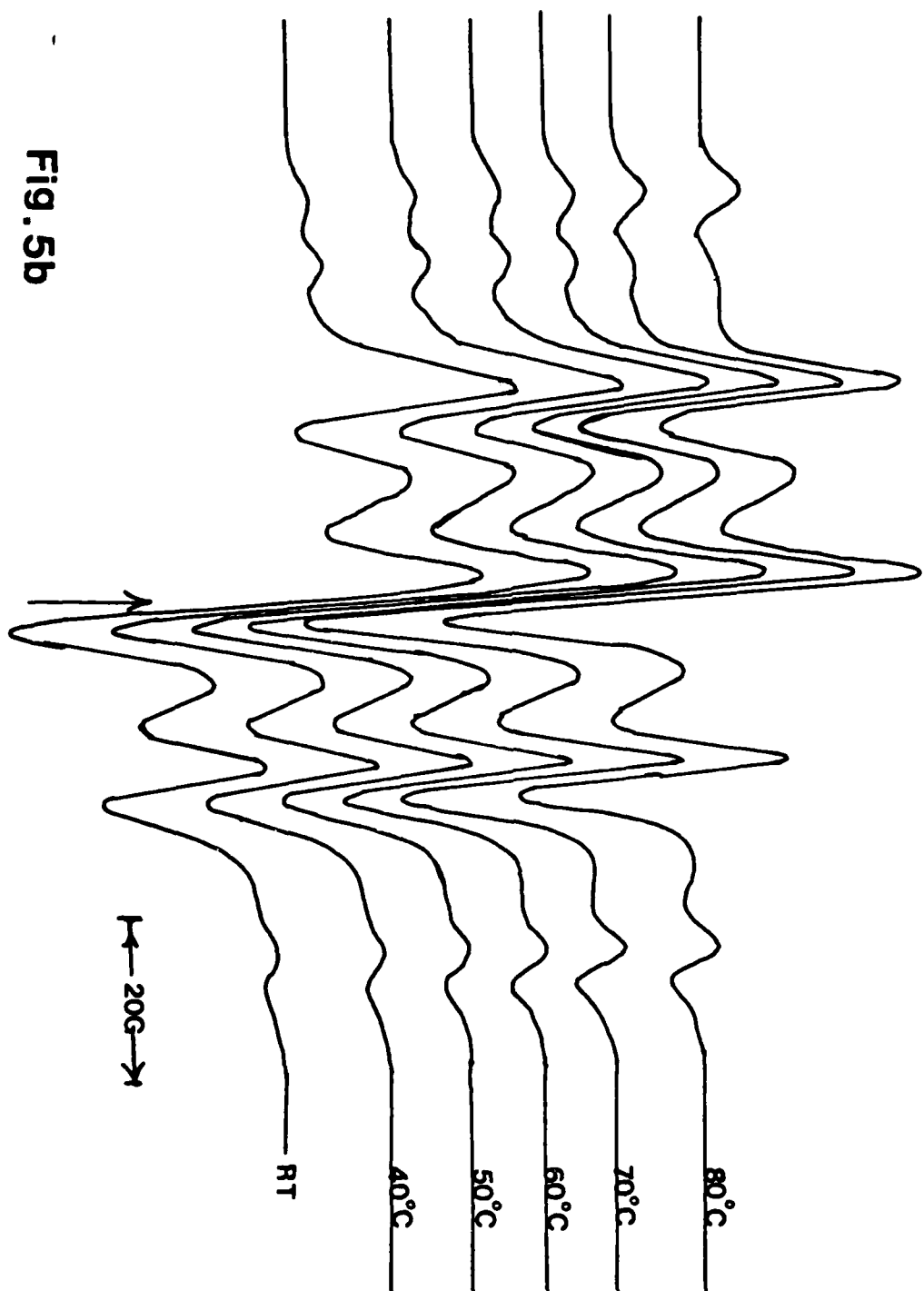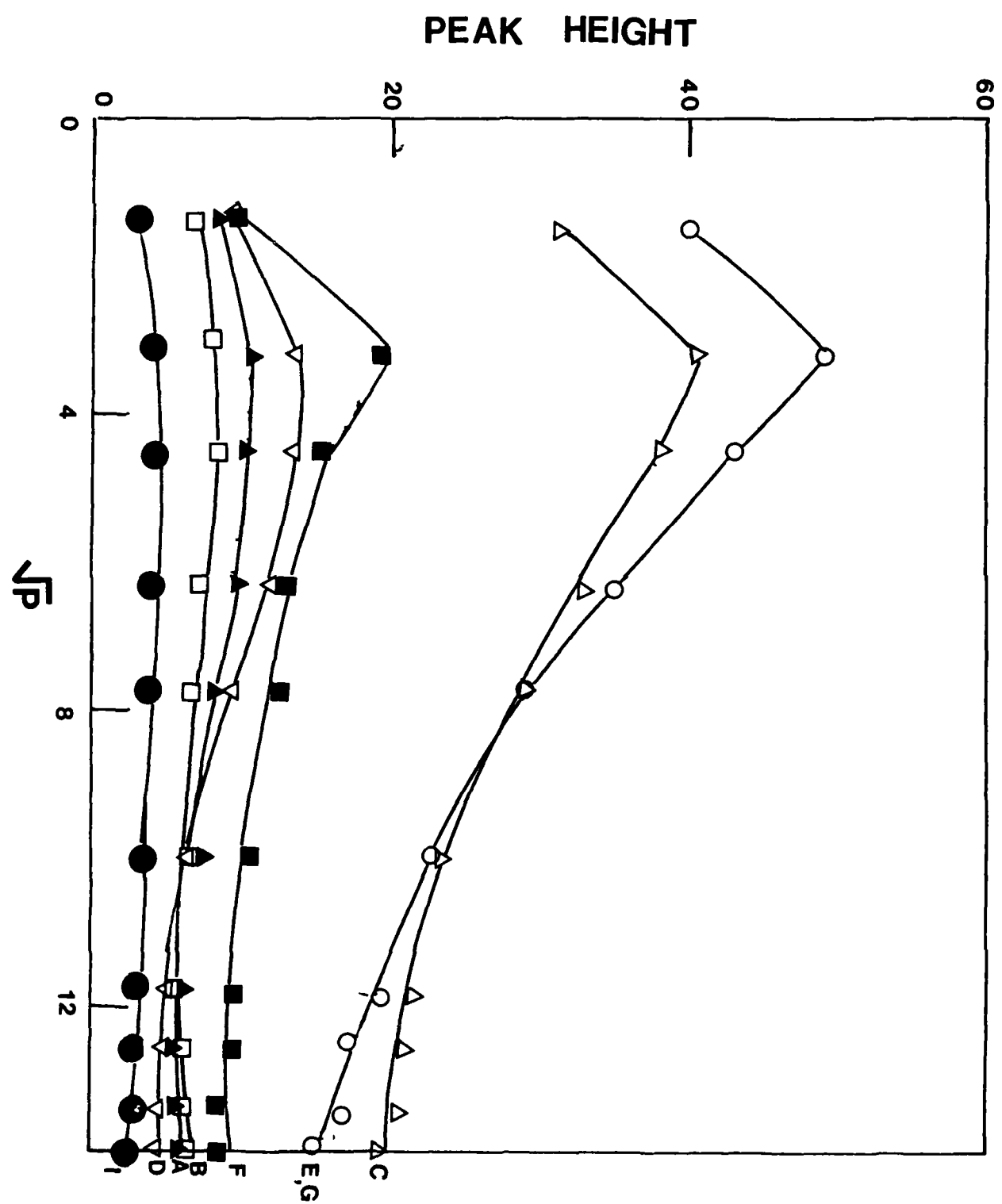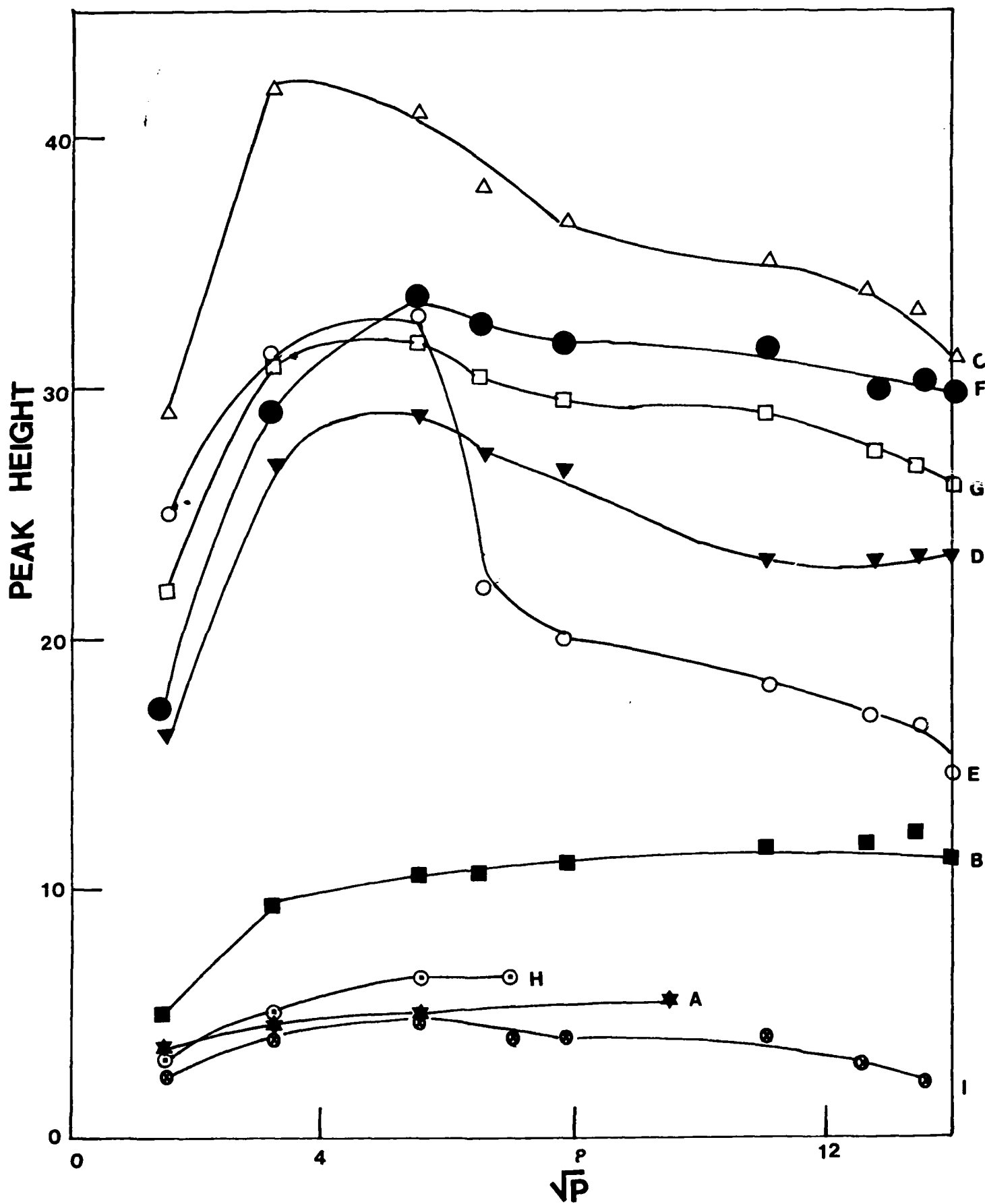
Fig.6b
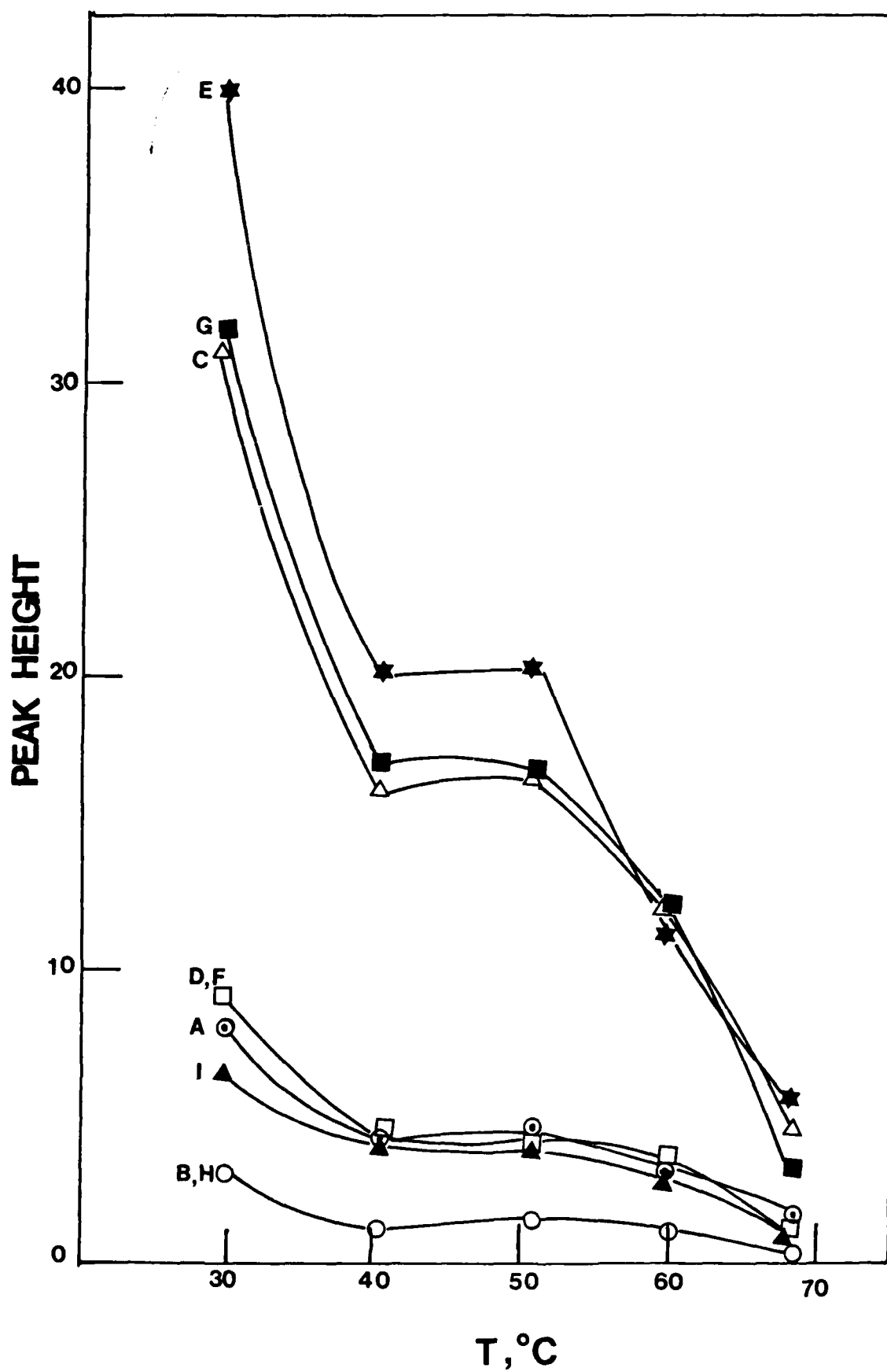
Fig.7a

Fig. 7b

Fig.8

Fig.9a

Fig.9b

Fig.10

END

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9-83

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